High-Nitrogen and High-Oxygen Chemistry

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Program Objectives

Discover, synthesize, characterize, and scale-up novel, highly energetic compounds

Technical Approach:

• Exploit synergism between theory and synthesis

• Use calculations to identify the most promising candidates and predict their properties

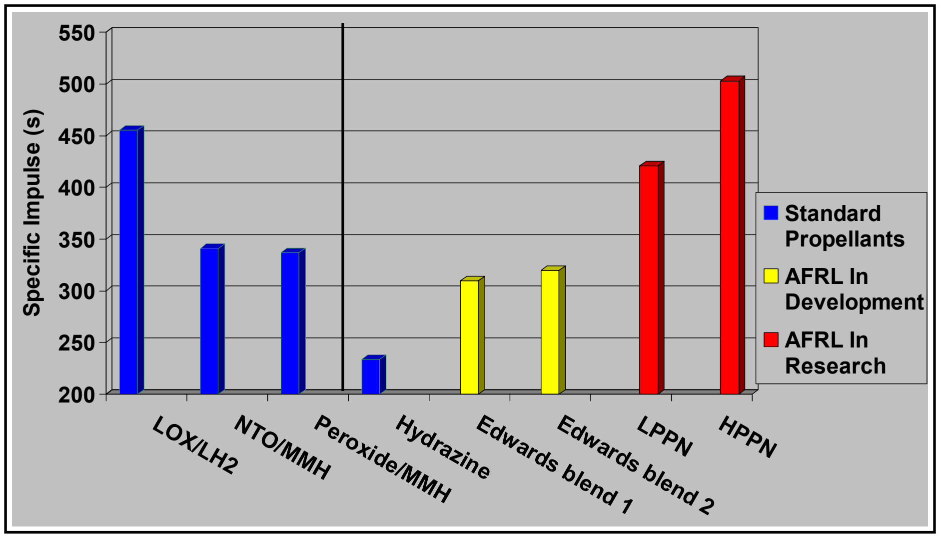
• Employ experimental expertise to design synthetic approaches, prepare novel compounds, and characterize products

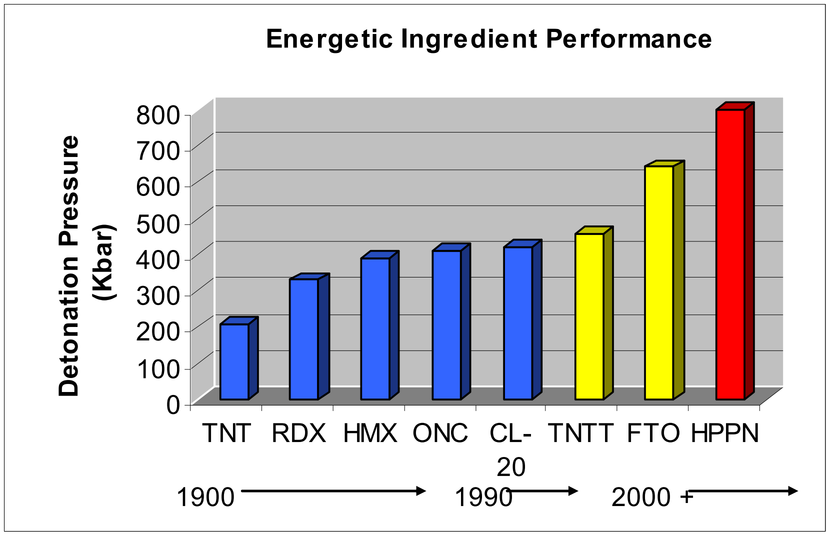
Outline

- Polynitrogen Chemistry
  - N_3^+ Chemistry
  - N_3NOF^+ and N_7O^+
  - New NMR Method
- Polyazide Chemistry
- Synthesis and Characterization of $FN(NO_2)_2$
- Stable Difluoramine Sources
- High-Oxygen Carriers and Oxidizer Balanced Ionic Liquids

Why are we interested in Polynitrogens?

The performance of polynitrogens as monopropellants would dwarf that of hydrazine, would greatly exceed even many bipropellants, and result in reduced signature





LPPN = Low performing polyN ($N_5^+N_3^-$);

HPPN = High performing polyN (cubic N_8)

Polynitrogens would also have great potential as high-performance explosives

Bulk Synthesis of N_3^+

- N_3^+ is a very promising candidate (is derived from a vibrationally stable radical and has high decomposition barrier)

- Studied F^- abstraction from FN_3 by strong Lewis acids

- Solved problem of synthesis and safe handling of FN_3 on a preparative scale, but found that N_α is a better donor than F

- HF addition to the FN_3-SbF_5 adduct, followed by N_2 elimination, results in the formation of $NH_2F_2^+$ salts

- Are working on synthesis of XeN_3^+ and its decomposition and on controlled photolytic decomposition of N_5^+ as potential methods for the production of N_3^+

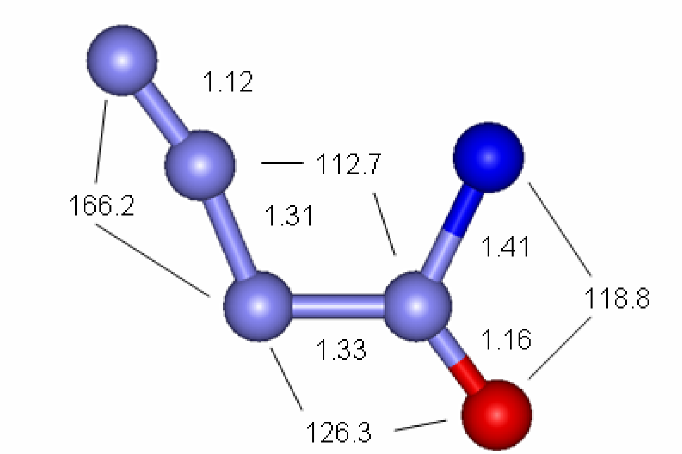
Syntheses of N_3NOF^+ and N_7O^+

- The reactions

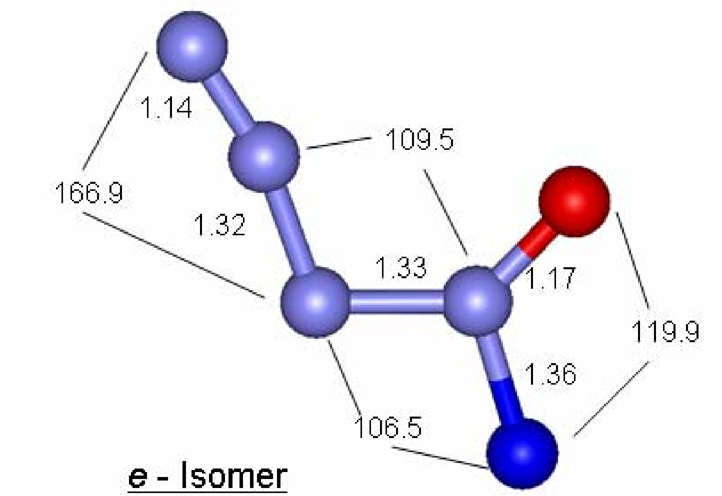
$$NOF_2^+SbF_6^- + HN_3 \longrightarrow N_3NOF^+SbF_6^- + HF$$

$$N_3NOF^+SbF_6^- + HN_3 \longrightarrow N_7O^+SbF_6^- + HF$$

were studied in HF at –78°C. $N_3NOF^+SbF_6^-$ was isolated and is stable up to ~ 20°C. N_3NOF^+ exists as both a *z*- and an *e*-isomer.



z - Isomer



e - Isomer

Natural Abundance ^{15}N NMR Spectroscopy

• Nitrogen NMR spectroscopy is crucial for the identification of novel polynitrogen compounds. Unfortunately, ^{14}N has a large quadrupole moment which broadens most signals to a point where they become unobservable, and the natural abundance of ^{15}N (0.36%) is too low and its relaxation time too long to allow the observation of ^{15}N spectra without ^{15}N enrichment. Prof. Taylor has developed a new NMR signal processing technique for the detection and enhancement of very weak NMR signals.

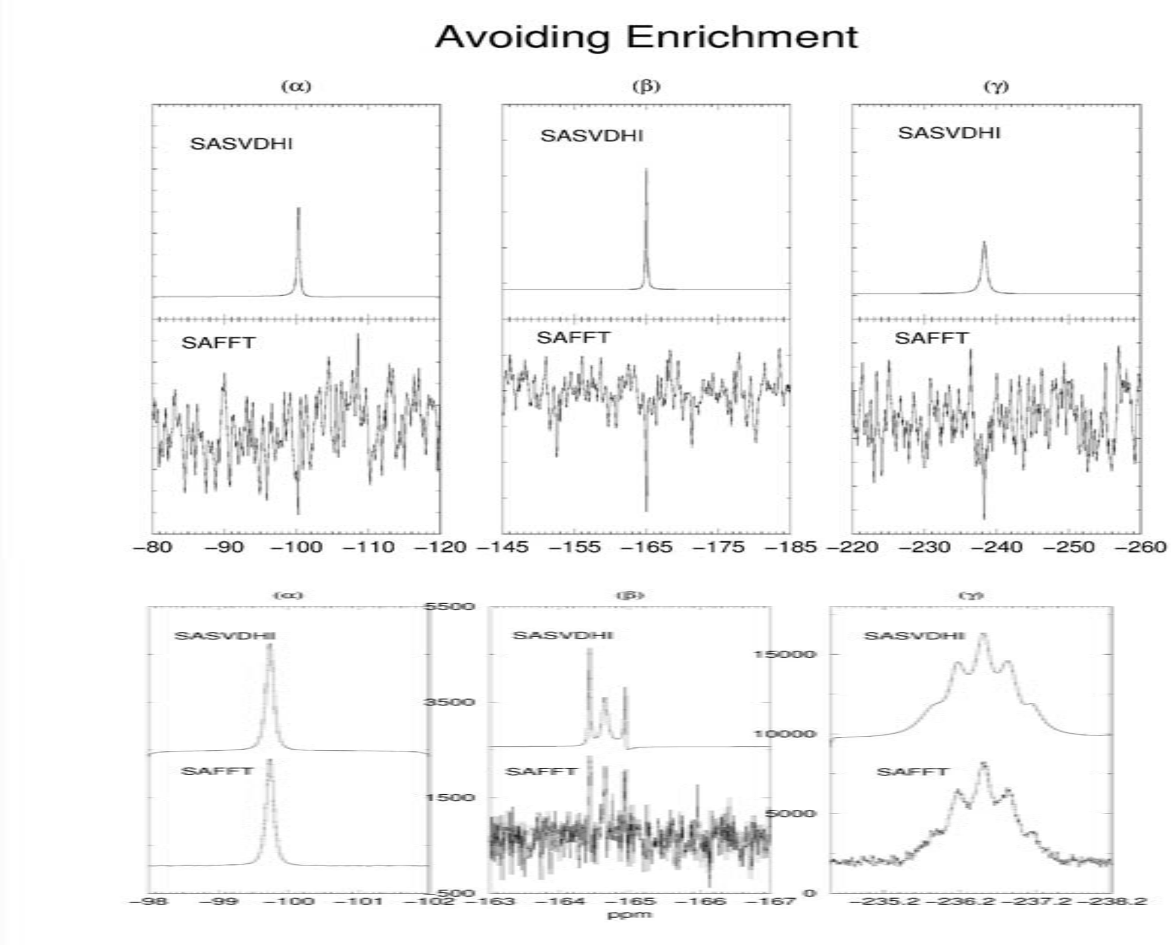
• The power of this new method was demonstrated for the natural abundance ^{15}N spectrum of N_5^+ which allowed the observation of the complete spectrum with an excellent signal to noise ratio. We were also able to observe the ^{14}N-^{15}N and ^{15}N-^{15}N couplings in a partially ^{15}N enriched spectrum.

Natural Abundance ^{15}N NMR Spectroscopy

- Same raw natural abundance ^{15}N data processed by the new and the conventional FT NMR methods for N_5^+.

New Method

Conventional FT NMR



New Method

Conventional FT NMR

Polyazide Chemistry

- One azido group contributes ~ 80 kcal/mol of endothermicity to a compound.
- Polyazides are highly energetic, sensitive materials which can be used for primary explosives. Typical example: $Pb(N_3)_4$.
- Have recently prepared and characterized numerous polyazides of S, Te, P, As, Sb, Ti, Mo and W, including spectacular compounds, such as $N_5^+[P(N_3)_6]^-$ and $N_5^+[B(N_3)_4]^-$.
- Results were published in a series of papers in Angewandte Chemie and Chemistry, A European Journal.

Synthesis of First Group 5 Binary Azides, $Nb(N_3)_5$, $Ta(N_3)_5$, $Nb(N_3)_5 \cdot CH_3CN$ and $[Nb(N_3)_6]^-$

- Synthesized $M(N_3)_5$ (M = Nb, Ta) in SO_2 according to

$$MF_5 + \text{exc. } TMSN_3 \xrightarrow{SO_2} M(N_3)_5 + 5\ TMSF$$

Both compounds are very sensitive and unstable. Raman spectra were recorded.

- Synthesized the adducts $M(N_3)_5 \cdot CH_3CN$ (M = Nb, Ta) according to

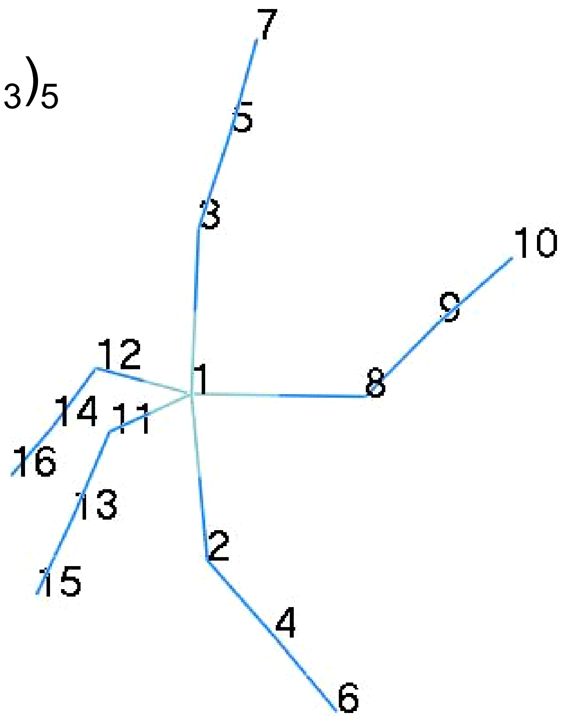
$$MF_5 + \text{exc. } TMSN_3 \xrightarrow{CH_3CN} M(N_3)_5 \cdot CH_3CN + 5\ TMSF$$

- Synthesized the anions $[M(N_3)_6]^-$ (M = Nb, Ta) according to

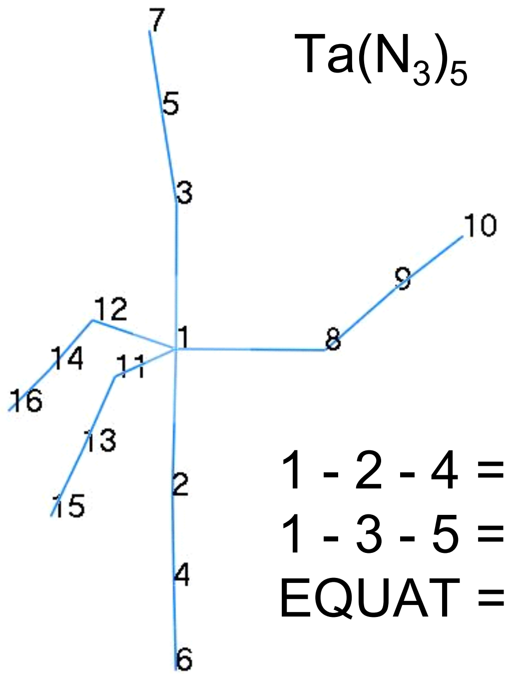
$$M(N_3)_5 + P(Ph)_4{}^+N_3{}^- \xrightarrow{CH_3CN} [P(Ph)_4][M(N_3)_6]$$

Structures of $Nb(N_3)_5$ and $Ta(N_3)_5$

$Nb(N_3)_5$



$Ta(N_3)_5$



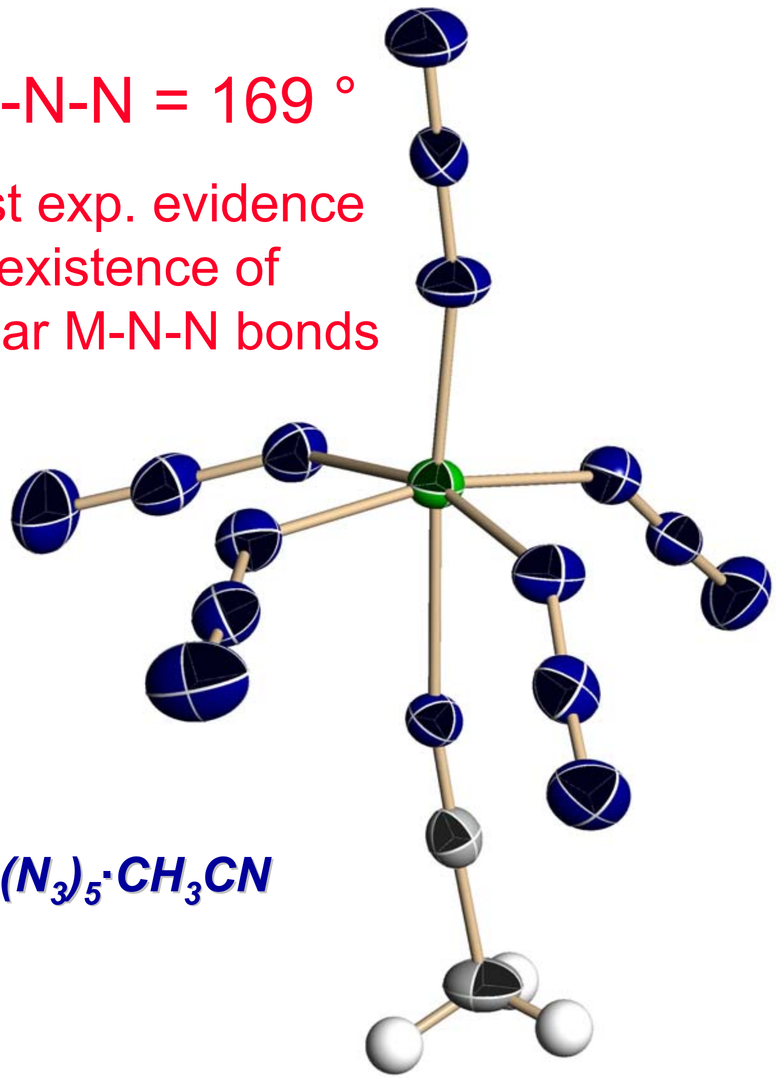
1 - 2 - 4 = 178 °
1 - 3 - 5 = 171 °
EQUAT = 137 °

- Contain both linear and bent M-N-N bonds
- Calculated structures are supported by observed Raman spectra

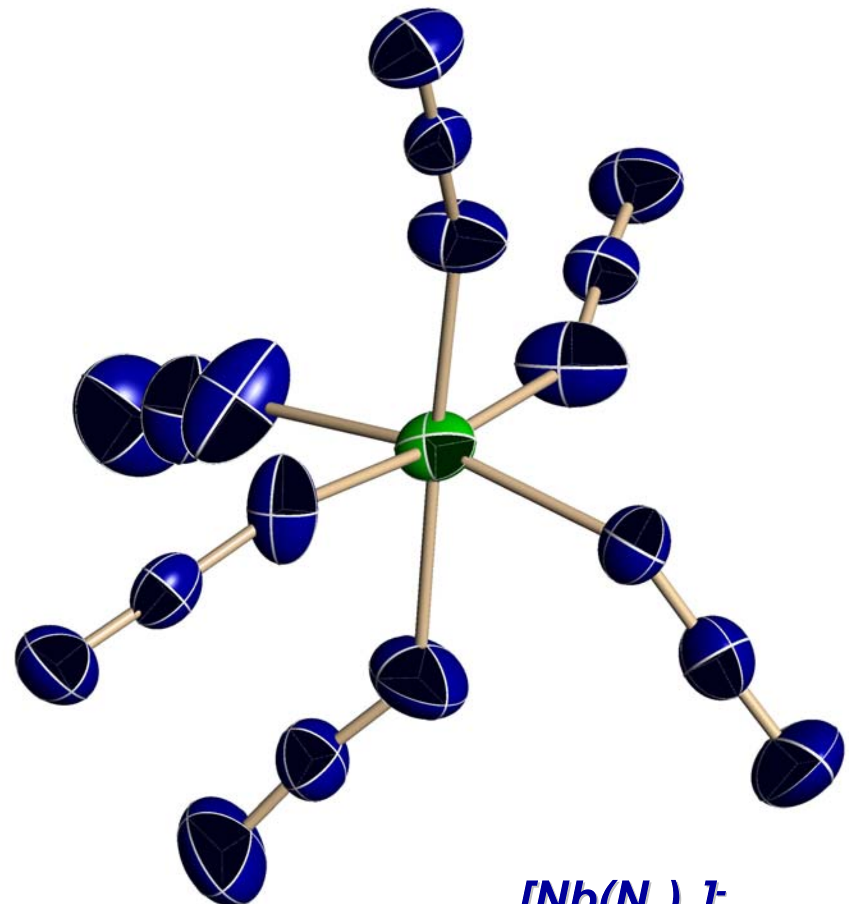
Crystal Structures of $Nb(N_3)_5 \cdot CH_3CN$ and $[Nb(N_3)_6]^-$

Nb-N-N = 169 °

First exp. evidence for existence of linear M-N-N bonds



$Nb(N_3)_5 \cdot CH_3CN$

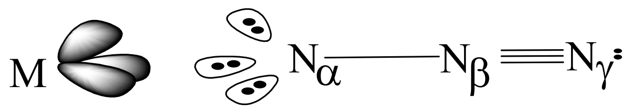


$[Nb(N_3)_6]^-$

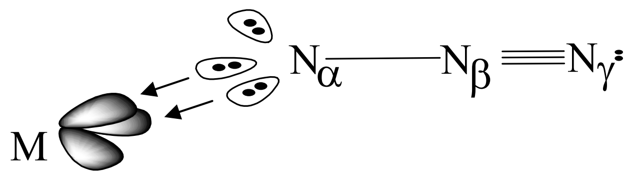
Explanation for Linear M-N-N Bonds

Bonding schemes for transition metal azides (from top to bottom): (i) ionic azide, showing for didactic reasons the azide ion in one of its asymmetric resonance structures and only some of the empty s_2d_{10} orbitals on M; (ii) strongly bent two-center/monodative bond; (iii) moderately bent two-center/bidative bond; (iv) linear two-center/tridative bond.

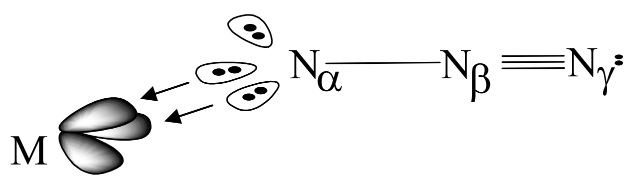
IONIC
M^+ N_3^-



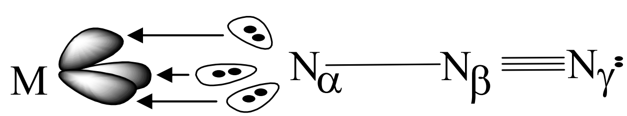
2c-1d
$(M{-}N_\alpha{-}N_\beta) = 109.5^o$



2c-2d
$(M{-}N_\alpha{-}N_\beta) = 125.5^o$

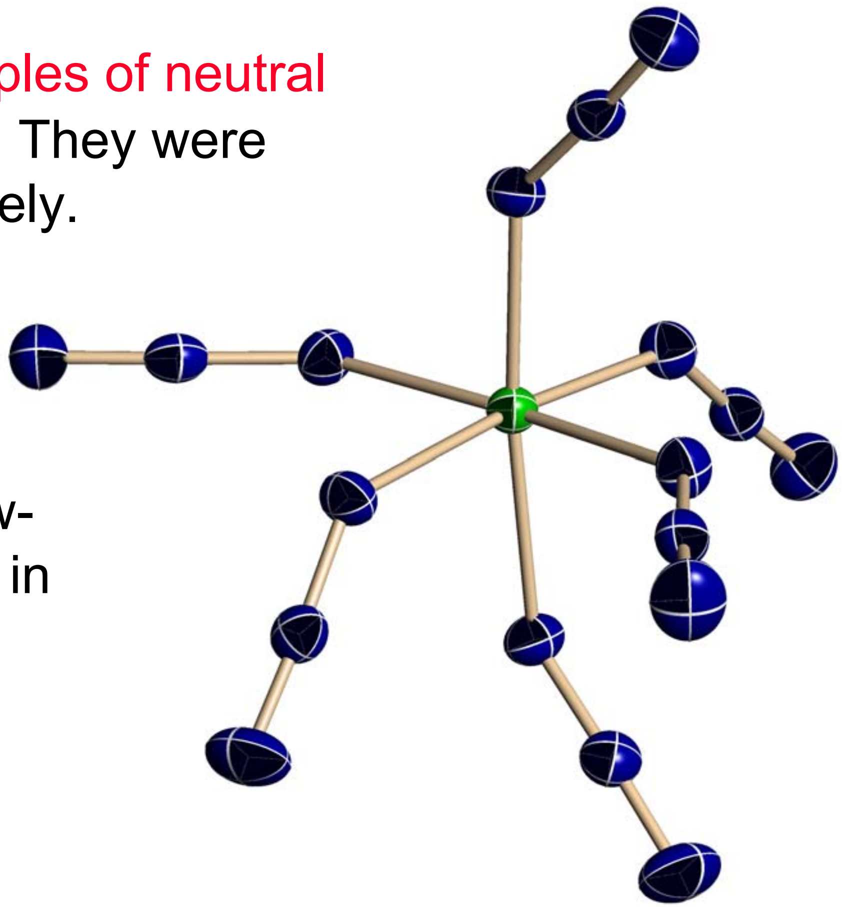


2c-3d
$(M{-}N_\alpha{-}N_\beta) = 180.0^o$



Molybdenum and Tungsten Azides

• $Mo(N_3)_6$ and $W(N_3)_6$ are the first examples of neutral hexaazides and binary Group VI azides. They were prepared from MoF_6 and WF_6, respectively.

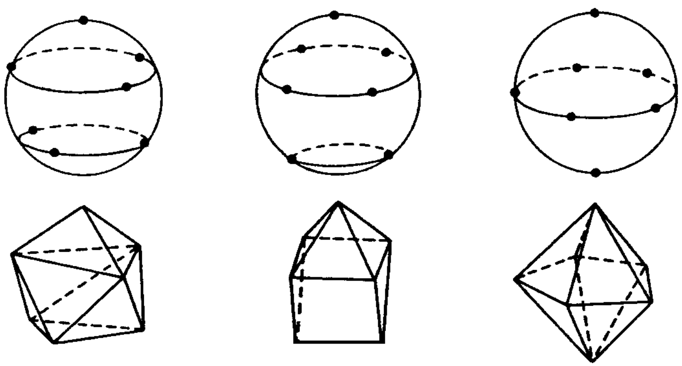


• Both compounds are highly shock sensitive and were characterized by low-temperature Raman spectroscopy and, in the case of $W(N_3)_6$, also by its crystal structure.

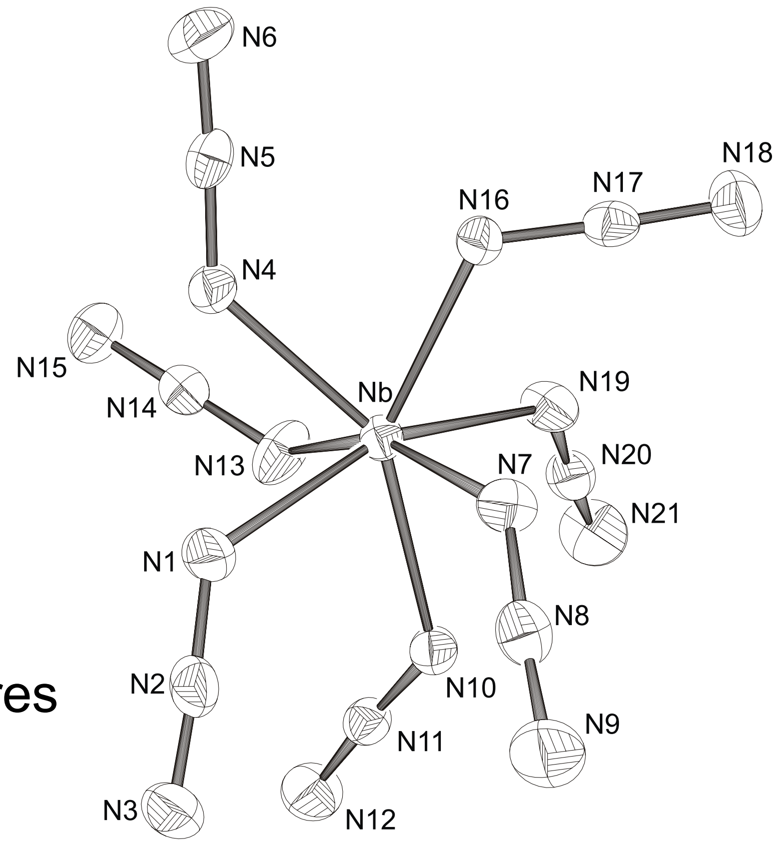
First Hepta-Azides

- Synthesized the $[W(N_3)_7]^-$, $[Mo(N_3)_7]^-$, $[Nb(N_3)_7]^{2-}$, $[Ta(N_3)_7]^{2-}$ anions

Possible arrangements for CN 7



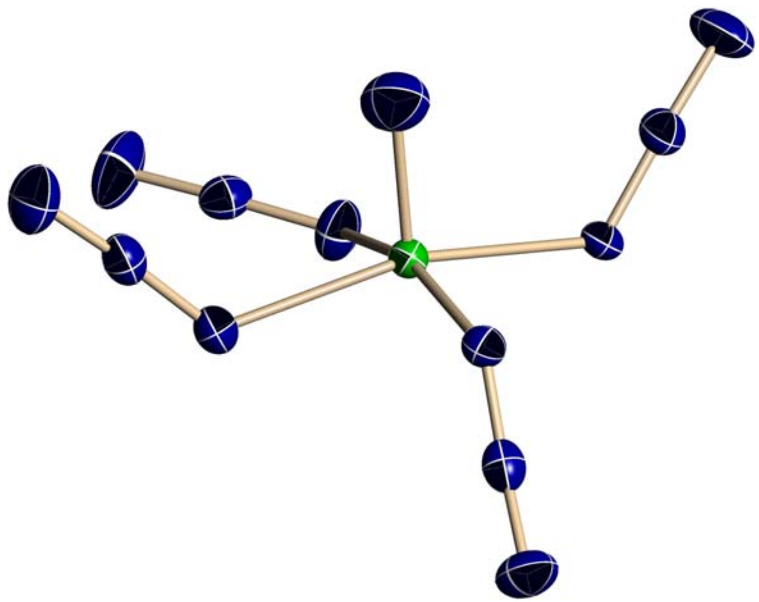
$M(N_3)_7$ anions have 2 : 4 : 1 structures



Synthesis of Nitrido-Azides

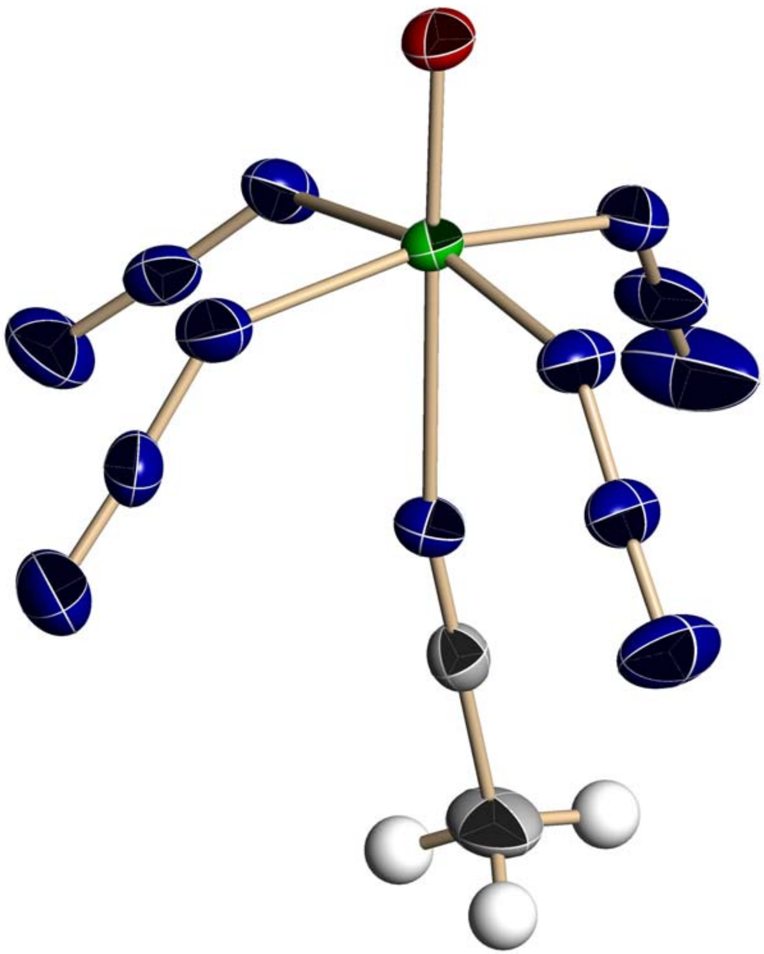
•Solid $[PPh_4][W(N_3)_7]$ and $[PPh_4][Mo(N_3)_7]$ are very sensitive compounds and decompose explosively. However, in solution at -30°C, partial N_2 evolution occurs with formation of nitrido-azides.

$$[PPh_4][M(N_3)_7] \longrightarrow [PPh_4][M(N)(N_3)_4] + 4\ N_2$$



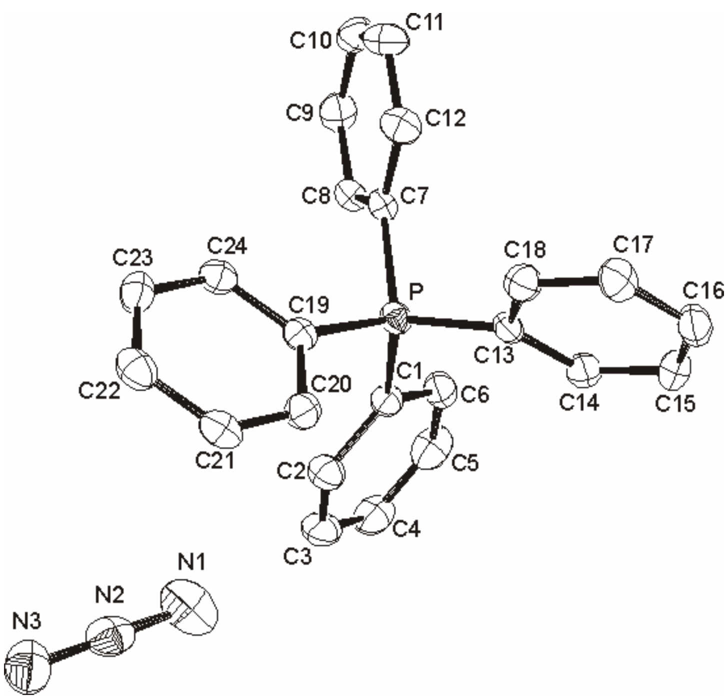
Oxoazides

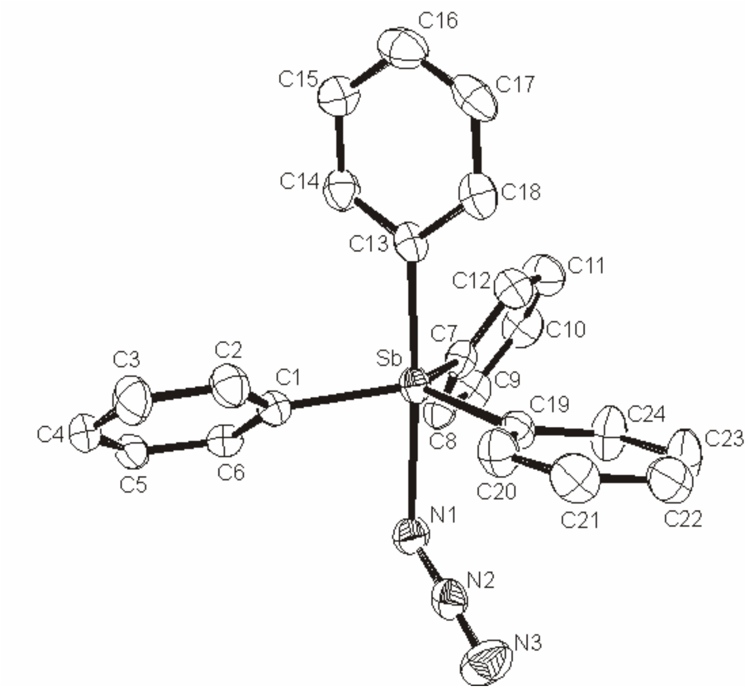
- $WO(N_3)_4$, [*cis*-$WO_2(N_3)_4]^{2-}$, [*trans*-$WO_2(N_3)_4]^{2-}$, $[MoO(N_3)_5]^{2-}$, and $[NbO(N_3)_5]^{2-}$, the first examples of transition metal oxoazides, were prepared and characterized by their crystal structures and vibrational spectroscopy
- [*trans*-$UO_2(N_3)_4]^{2-}$, the first example of an actinide oxoazide, was also prepared and characterized by its crystal structure



Transition from Ionic to Covalent Azides

- Obtained crystal structures of $M(Ph)_4N_3$ where M = P, As, Sb
- $P(Ph)_4N_3$ and $As(Ph)_4N_3$ are ionic, while $Sb(Ph)_4N_3$ is covalent





Synthesis and Characterization of $FN(NO_2)_2$

- Prepared $NF_4^+N(NO_2)_2^-$ at low temp in SO_2 solution

$$NF_4^+SbF_6^- + K^+N(NO_2)_2^- \longrightarrow KSbF_6 + NF_4^+N(NO_2)_2^-$$

and decomposed it according to:

$$NF_4^+N(NO_2)_2^- \longrightarrow NF_3 + FN(NO_2)_2$$

- $FN(NO_2)_2$ was characterized by low-temperature multinuclear NMR spectroscopy and is unstable at room temperature

- Efforts are in progress to isolate it in pure form

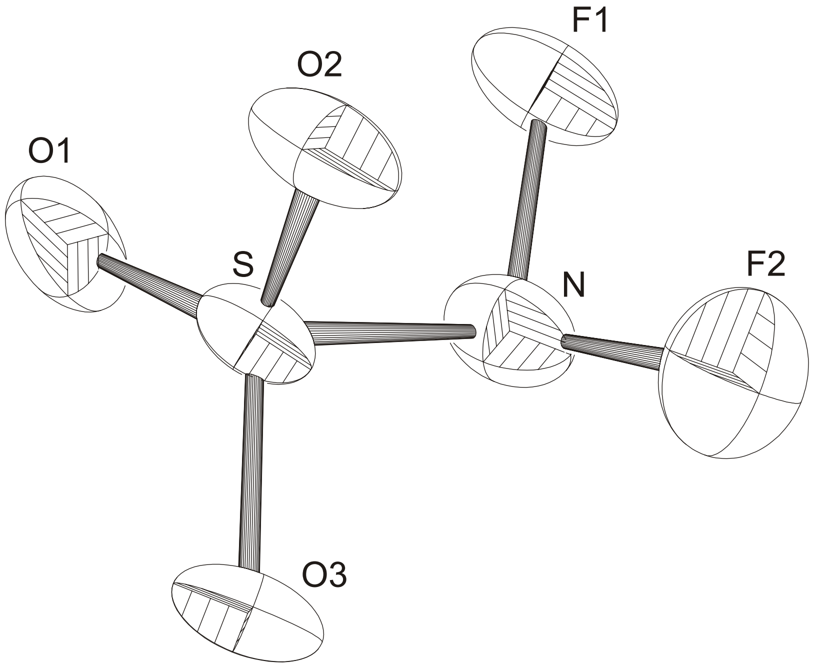
$SO_3NF_2^-$, a *Stable Difluoramine Source*

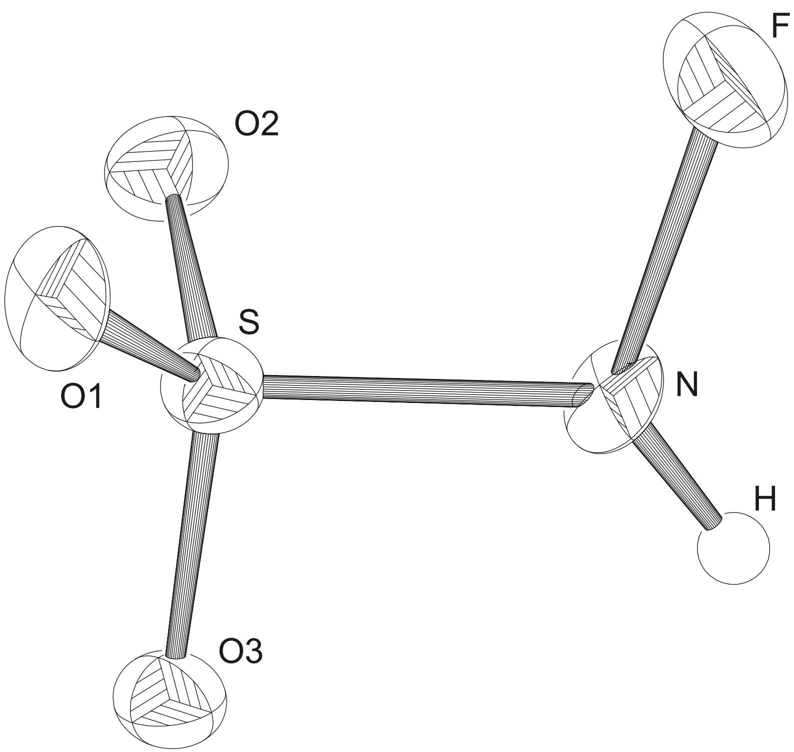
- Stable, safely storable sources for the generation of the highly explosive HNF_2 are of great interest for the synthesis of *gem*-bis-difluoramino compounds.
- In previous work, we have demonstrated the potential of $(C_6H_5)_3CNF_2$ for this application. However, the synthesis of $(C_6H_5)_3CNF_2$ requires pressurizing N_2F_4 in chlorobenzene solution and mercury and is cumbersome and dangerous.
- We have searched for a more convenient and accessible stable HNF_2 source. We found that alkali metal salts of the previously unknown $SO_3NF_2^-$ anion can be prepared by a simple, one-step, direct fluorination of the sulfamate anion in water

$$M^+SO_3NH_2^- + 2\ F_2 \longrightarrow M^+SO_3NF_2^- + 2\ HF$$

The $SO_3NF_2^-$ and related SO_3NHF^- salts were characterized by their crystal structures, vibrational and NMR spectroscopy, and theoretical calculations, and shown to be excellent stable reagents for converting carbonyl groups into *gem*-bis-NF_2 groups.

Crystal Structures of $SO_3NF_2^-$ and SO_3NHF^-





High-Oxygen Carriers and Ionic Liquid Propellants

- Ionic liquids have great potential for liquid propellants (Christe, Drake, pending US Patent).

- Because the bulky cations require large amounts of oxygen for complete combustion and high performance, there is a great need for high-oxygen carrying anions.

- We have investigated the usefulness of the tetranitrato-borate and tetranitrato-aluminate anions for these applications, and their ability to form room temperature ionic liquids.

- We have prepared and characterized numerous tetranitrato-borate salts. Although 1-ethyl-3-methyl imidazolium tetra-nitrato-borate forms a low freezing (-30 °C) ionic liquid, its thermal stability of 60 °C is insufficient for practical applications.

High-Oxygen Carriers and Ionic Liquid Propellants

- Replacement of $[B(NO_3)_4]^-$ by $[Al(NO_3)_4]^-$ was highly successful.
- We prepared and characterized 1-ethyl-3-methyl imidazolium tetranitrato-aluminate:

    Thermal stability (DSC): >200 °C

    Freezing Point = -30 °C

    ρ = 1.508 g/cm^3

    Dropweight, negative at 10 kg·cm

    Friction, 24 kg

    Calcd Isp = 261 sec

- We are presently preparing tetrazolium tetranitrato-aluminates with predicted Isp values of 280-290 sec.

Conclusions

- Excellent progress is being made in the area of polynitrogen chemistry (N_3^+, N_3NOF^+, N_7O^+).
- A large number of novel polyazides, nitrido-azides and oxo-azides were prepared and characterized.
- A new NMR data processing method was developed and applied to N_5^+ which allows the observation of ^{15}N NMR spectra in natural abundance.
- The new $FN(NO_2)_2$ molecule was synthesized and characterized.
- The novel $M^+SO_3NF_2^-$ salts were synthesized and characterized, and their usefulness for preparing *gem*-bis-difluoramino compounds was demonstrated.
- High-oxygen carrying anions hold great promise for oxidizer-balanced, ionic liquid propellants.